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Spray-on thermoelectric energy harvester

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ABSTRACT

Thermoelectric (TE) thin films have promise for harvesting electrical energy from waste heat. We demonstrate TE materials and thermocouples deposited by aqueous spray deposition on glass. The n-type material was CdO doped with Mn and Sn. Two p-type materials were investigated, namely PbS with co-growth of CdS and doped with Na and Na_2CoO_4. Seebeck coefficients, resistivity, and power generation for thermocouples were characterized.

INTRODUCTION

Thin-film thermoelectric energy harvesters have been suggested for long-flight-duration un-manned aerial vehicles [1]. Temperature gradients of ~1 deg C per cm occur along aircraft skins [2]. Waste heating of vehicle exhaust systems can give surface lateral temperature gradients exceeding 2 deg C per cm [3]. Such offer opportunity for energy harvesting using thin film thermocouples applied as paint-like coatings. This paper investigates thermoelectric thin films prepared by an aqueous spray process.

Power generation from stoves and lamps [4,5] has potentially large market and significant humanitarian impact in developing countries, for charging Li batteries and operating medical devices during night time hours. Such a TE power generator is commercially available [6]. The ability to spray-coat complex objects, whose surfaces have temperature gradients resulting from standard use, has advantage of distributed low-cost manufacturing.

CdO is the n-type thermoelectric metal oxide material considered here [7-9]. The first p-type thermoelectric material we considered was the metal chalcogenide PbS, which we had grown previously for infrared detection [10]. We doped with Na and co-grew CdS nano-inclusions [11]. However, difficulties in co-processing PbS on the same substrate with CdO led us to consider Na_2CoO_4 (NCO) [12, 13]. NCO and CdO are both stable against oxidation in air. For purposes of mass production of useful power generators, we explored photolithographic patterning.

EXPERIMENTAL DETAILS

The aqueous-spray thin-film growth method is Streaming Process for Electrodeless Electrochemical Deposition (SPEED). Films were grown in ~ 1 cm wide stripes on a 50 mm x 50 mm x 1.1 mm borofloat glass substrate in p- and n-type pairs. The chemistry for growing CdO films by SPEED is similar to that for SnO_2 [13]. A little Sn promotes growth of CdO. Mn was added a dopant [9]. Mn is a group 7B element, and in its 4^+ oxidation state it should act as a donor. Its size mismatch should reduce thermal conductivity. Cations from $CdCl_2$, $SnCl_4$, and $MnCl_2$ were complexed with organic solvents in ~20% water. Nano-crystalline growth was carried out at substrate temperatures 300 - 400^o C.

PbS film was grown [10] with dissolved $NaNO_3$, and $Cd(NO_3)_2$ salts to dope with Na and co-grow CdS inclusions [11]. For NCO film, $NaNO_3$, $Co(NO_3)_2$, and urea were dissolved stoichiometrically in water. Na and Co ions were complexed with mixed organic solvents to obtain a clear solution that was sprayed on heated substrate at 300 to 400^o C.

Film thickness was measured by contact profilometry. Resistivity ρ was determined by 4-pt probe method. Seebeck coefficients $S = -dV/dT$ were measured using a homemade resistive heater clamp providing high temperature T_h up to 100^o C. The low temperature T_c was maintained near room temperature. Thermocouples were formed by electrically connecting ends of strips made from n- and p-type materials. The thermoelectric length was ~ 44 mm. For single thermocouples, open circuit voltage V_{oc} was measured using a digital voltmeter. Short circuit current I_{sc} was measured using a nano-ammeter. The maximum achievable power was estimated as $I_{sc} * V_{oc}$.

Photolithographic patterning was achieved by first spinning negative-tone photoresist, then UV-exposing in a mask aligner through a shadow mask in 3 mm x 50 mm stripes, developing, and de-scuming in oxygen plasma. Then AlN was reactively sputtered over the whole substrate, followed by lift-off in acetone. Then one of the thermocouple partner materials was blanket deposited by SPEED, followed by lift-off in KOH. The process was repeated to deposit the stripes of the partner material in the gaps between the first.

RESULTS

Table I presents the growth conditions and thermoelectric properties of the films, which are arranged in n-p pairs grown on the same substrate. Annealing increases conductivity via grain growth. PbS was annealed in sulfur vapor to avoid oxidation and loss of sulfur, and this significantly lowers PbS resistivity (Table I). However, annealing in sulfur turns CdO into an insulator. This led us to consider the oxide NCO as the p-type partner for CdO.

Table I. Thermoelectric films grown and studied. The n- and p-type films grown side by side on the glass substrate are arranged in pairs.

Film	Growth Temp. (°C)	Annealed	Resistivity (Ω-cm)	Seebeck coeff. (μV/K)
n-CdO	400	No	0.032	-40
p-PbS	300	No	720	+688
n-CdO	400	400° C, 30 min in Sulfur	insulating	N/A
p-PbS	300	400° C, 30 min in Sulfur	1	+563
n-CdO	400	500° C, 1.5 hr in air	0.23	-72.5
p-NCO	300	500° C, 1.5 hr in air	34	+20.0
n-CdO	400	500° C, 1.5 hr in air	1.2	-85.7
p-NCO	400	500C, 1.5 hr in air	8.2	+125

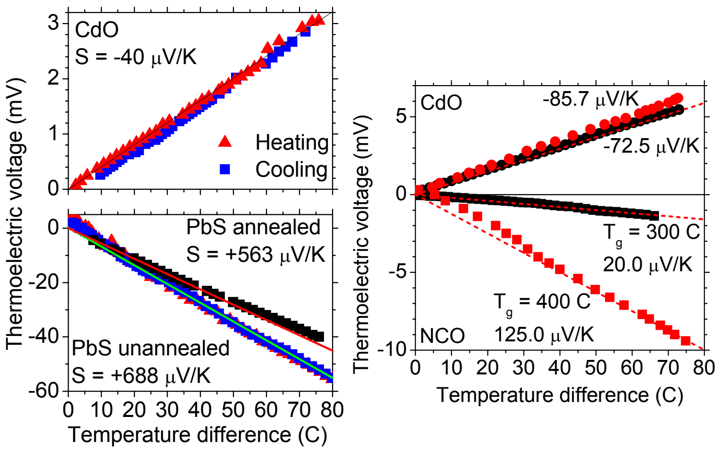

Figure 1. Determination of Seebeck coefficients for (left) CdO and PbS film pairs and (right) for CdO and NCO film pairs.

Figure 1 (left) presents thermoelectric voltage measured on the paired CdO and PbS films. Heating and cooling curves are similar indicating good temperature sensor placement. The voltage measured between hot and cold ends is positive for the n-type CdO and increases linearly with temperature difference. The Seebeck coefficient compares well with values for spray-deposited films of CdO:Zn and CdO:Mn [9] and with sintered CdO pellets [8]. The S values for PbS are quite high, though the resistivity is also very high. Annealing in sulfur reduces the Seebeck coefficient slightly by a factor of 1.22, while the resistivity (Table I) is reduced by a factor of 720. Thus, annealing in sulfur vapor improves the power factor S^2/ρ of the PbS film by 480 times, but this annealing changed the CdO on the substrate to thermoelectrically useless insulator.

Figure 1 (right) presents the Seebeck-coefficient determination for two NCO films grown at different temperatures. The film grown at 400° C has 6.25 times higher Seebeck coefficient than one grown at 300° C, while the resistivity (Table I) is 4.1 times lower. Thus, the power factor is improved by a factor of 160 by growing hotter.

The CdO stripes paired with the two NCO films were both grown at 400° C and they have nearly the same Seebeck coefficient. The value is twice higher than found previously in Figure 1. The only difference in the method of deposition is the shadow mask material, aluminum in the first case, stainless steel in the second, so that diffusion of impurities may be a factor. The resistivities of the two CdO samples in Figure 2 also differ by a factor of 5 (Table I).

Figure 2 presents the open circuit voltage V_{oc} (solid symbols) and short circuit current I_{sc} (open symbols) measured at the free cold ends of single thermocouples for the three good n-p pairs in Table I. The films are distinguished by symbol color. The numbers in parentheses after NCO in the legend indicate the film growth temperature. Figure 2 allows an estimate of the achievable power $I_{sc}*V_{oc}$. At a temperature difference of 75 C, we have for CdO/NCO(300), CdO/PbS, and CdO/NCO(400) the values 0.32, 0.07, and 1.33 nW. Considering that the heater power was ~10 W, the efficiencies are of course very small, less than 10^{-8} % for the best CdO/NCO pair. Higher temperature would improve this efficiency.

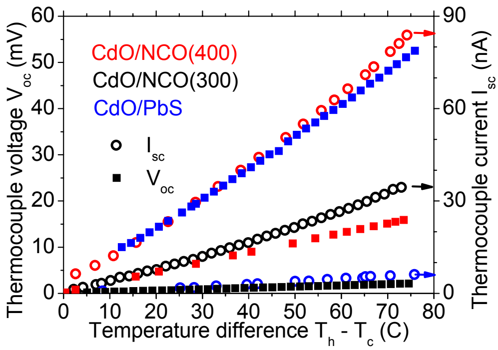

Figure 2. Open circuit voltage and short circuit current for three thermocouples.

SUMMARY AND DISCUSSION

This paper reported on CdO/PbS and CdO/Na_2CoO_4 thin-film thermocouples deposited by aqueous spray deposition on glass. Seebeck coefficients, resistivity, and power generation were characterized for films with different growth temperatures and annealing treatment.

Power output is expected to rise rapidly with thermoelectric length *l* (distance between hot and cold points) up to ~0.5 mm, beyond which it falls slowly as 1/*l* [15]. Since spray deposited films can be deposited to only a few micron thicknesses, they seem best suited for exploiting lateral temperature differences on non-uniformly heated surfaces. The thicker substrate would contribute more than the thin film to thermal conduction, so that the thermal conductivity that appears in the denominator in the usual ZT figure of merit for thermoelectrics would seem to be irrelevant for the considered implementation.

Lateral temperature gradients on substrates such as aircraft skins and vehicle exhaust systems are just a few degrees per cm, so that useful temperature gradients would require thermoelectric lengths of order 50 cm, reducing harvestable power by a factor of 1000 from what would be obtained for optimum *l*. This might be compensated by the large surface areas in certain applications that could host a large number thermocouples deposited as a patterned paint.

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